#### **PCT**

### WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



#### INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :		(11) International Publication Number: WO 99/393
H01L 21/02	A2	(43) International Publication Date: 5 August 1999 (05.08.
(21) International Application Number: PCT/US (22) International Filing Date: 29 January 1999 (20)		BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, C GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, F LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, M MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,
(30) Priority Data: 60/073,068 09/238,708 30 January 1998 (30.01.98) 28 January 1999 (28.01.99)  (71) Applicant: TRUSTEES OF PRINCETON UNIV	τ	(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European pat (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
<ul> <li>[US/US]; P.O. Box 36, Princeton, NJ 08544-0036</li> <li>(72) Inventors: STURM, James, C.; 3R Magie Apt., Facu Princeton, NJ 08540 (US). WU, Chung, Chih No. 43, Sec.2, Shin-Hal Road, Taipei (TW). Duane; 22 Kilmer Drive, Ewing, NJ 08638 (US). H</li> </ul>	lty Roa ; 12F– MARC	Published  Without international search report and to be republish upon receipt of that report.
Thomas, R.; 214G Halsey Street, Princeton, NJ 085  (74) Agent: FRISCIA, Michael, R.; Friscia & Nussbar University Plaza, Hackensack, NJ 07601 (US).	540 (US	

(54) Title: FABRICATION OF ORGANIC SEMICONDUCTOR DEVICES USING INK JET PRINTING

#### (57) Abstract

A method of fabricating semiconductor devices using ink-jet printing is provided to directly deposit patterned polymer films to create OLEDs and other semiconductor devices. The luminescence of poly-vinylcarbazol (PVK) films, with dyes of coumarin 6 (C6), coumarin 47 (C47), and nile red was similar to that of films of the same composition deposited by spin-coating. Light emitting diodes with low turn-on voltages were also fabricated in PVK doped with C6 deposited by ink-jet printing.

#### FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia	
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia	1
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal	
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland	- 1
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad	
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo	
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan	1
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan	- 1
BF	·Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey	
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago	i
BJ	Benin	Œ	Ireland	MN	Mongolia	UA	Ukraine	
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda	
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America	
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan	
CF	Central African Republic	JP	Japan	NE	Niger	VN ,	Viet Nam	
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia	
СН	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe	
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand			
CM	Cameroon		Republic of Korea	PL	Poland			
CN	China	KR	Republic of Korea	PT	Portugal			
CU	Cuba	KZ	Kazakstan	RO	Romania			
cz	Czech Republic	LC	Saint Lucia	RU	Russian Federation			
DE	Germany	LI	Liechtenstein	SD	Sudan			
DK	Denmark	LK	Sri Lanka	SE	Sweden			
EE	Estonia	LR	Liberia	SG	Singapore			
	Listoma				• •			
1								
1								

-1-

# FABRICATION OF ORGANIC SEMICONDUCTOR DEVICES USING INK JET PRINTING

# SPECIFICATION BACKGROUND OF THE INVENTION

5

10

15

20

25

30

#### FIELD OF THE INVENTION

The invention relates to methods of making semiconductor devices using organic active layers. The method involves the direct deposition of patterned luminescent doped polymers by ink jet printing, and the fabrication of organic light emitting diodes (OLED's) and other semiconductor devices from ink-jet-deposited organic films.

#### **RELATED ART**

Recently, there has been increased interest in light emitting diodes made from organic polymers because of their potential low cost and potential applicability to color flat panel displays. The organic materials are typically deposited by spin-coating (in the case of polymer materials), or by evaporation (in the case of small organic molecules). In either case, the single material covers the substrate so that only devices of a single color can generally be fabricated. The straightforward integration of multiple organic layers (for the fabrication of red, green, and blue emitters for color displays) would require the patterning of the individual organic layers. Because of their solubility in and sensitivity to aqueous solutions and many solvents, such patterning of organic materials by conventional photoresist and wet processing techniques is difficult. Efforts to date to integrate organic light emitting diodes (OLED's) from materials which emit different colors on the same substrate have patterned them only indirectly (through the use of cathodes evaporated through shadow mask as dry-etch masks), or avoided the issue all together by putting the three devices on top of each other (relying on shadow masks to pattern the organics so that contacts to the multiple layers may be made).

Different colors are obtained in light emitting diodes by placing red, green and blue emitting materials in proximity to each other using photoresist patterning and

-2-

etching techniques to transfer the photoresist pattern into the polymer; however, such photoresist techniques are inapplicable to organic materials because the chemicals uses for the photoresist process are incompatible with organic materials. Similarly, patterning subsequent layers on top of the organic (such as metal contacts) is difficult for the same reason. Vacuum deposited organic layers and metals may be patterned by evaporating them through shadow masks, but this technology is difficult to extend to large areas.

5

15

Other efforts using ink-jet printing in the fabrication of semiconductor devices include:

10 U.S. Patent 4,736,704 to <u>Henninger</u>, deposits solder masking to a circuit board using an ink-jet like technique.

U.S. Patent 5,132,248 to <u>Drummond, et al.</u>, disclose the deposition of materials on a substrate by ink-jet printing. The materials are formulated as colloidal suspensions. The materials discloses are metals, alloys, dielectrics and superconductors.

However, none of these previous efforts relate directly to the deposition of organics on a substrate by ink-jet printing.

-3-

#### **OBJECTS AND SUMMARY OF THE INVENTION**

It is an object and advantage of the invention is to provide a method which enables the use of the direct deposition of patterned semiconducting polymers, including luminescent polymers and doped polymers by ink jet printing.

Another object of the present invention is to provide for the successful fabrication of organic light emitting diodes and other semiconductor devices from inkjet-deposited organic films.

5

10

15

20

25

Still another object and advantage of the invention is to form devices of the class described with commercially available ink-jet printers.

A further object and advantage of the invention is the provision of a method using ink-jet printers where the ink cartridges are replaced with polymer solutions.

Even another object of the invention is to provide a method that employs a hole-transport polymer poly-vinylcarbazol (PVK) and light emitting dyes coumarin 6 (C6), coumarin 47 (C47) and nile red dissolved into a chloroform solution.

A still further object and advantage of the invention is the provision of a method and apparatus which employs ink-jet printing where, after deposition, the chloroform evaporates leaving a doped polymer material.

An additional object of the present invention is to provide a resultant product from solutions having typical concentrations of PVK dissolved in chloroform of 10g/l, and dye dissolved in chloroform of 0.1g/l to yield on the order of 1% dye in the PVK.

An additional object of the present invention is the provision of a process for forming organic light emitting diodes and other semiconductor devices.

Even an additional object of the invention is to provide a process of forming organic light emitting diodes and other semiconductor devices using ink-jet printing.

Still even an additional object of the present invention is the ability to use inkjet printing to deposit organic materials on a substrate.

Yet an additional object of the present invention is to provide a process using ink-jet printing for deposition of luminescent polymers.

A further object of this invention is the provision of a process using ink-jet printing for fabricating top and bottom contacts onto a substrate.

\_4\_

A still further object of the invention is the provision of a process for ink-jet fabrication of active or passive matrices.

The methods of this invention involve the direct deposition of patterned luminescent doped polymers by ink jet printing, and the fabrication of OLED's from ink-jet-deposited organic films. OLED's formed in accordance with this invention may have multiple organic layers on top of one another. Not all layers need be luminescent.

#### -5-BRIEF DESCRIPTION OF THE DRAWINGS

Other important objects and features of the invention will be apparent from the following Detailed Description of the Invention taken in connection with the accompanying drawings in which:

- Fig. 1(a) is an optical micrograph of ink jet printed dots from above, and Fig. 1(b) is plot of the surface profile of a dot.
  - Fig. 2 is a photograph of ink-jet printed luminescent polymer letters of nile red doped PVK excited by an ultraviolet lamp. The letters ink-jet printed using "bold" mode.
- Fig. 3 is a plot of the photoluminescence spectra of ink-jet printed and spin-coated PVK film doped with C47 (blue), C6 (green), and nile red.
  - Fig. 4 is a plot of current vs. voltage for devices fabricated with ink-jet printed and spin-coated films of PVK doped with C6.
    - Fig. 5 is a plot of luminescence vs. current for two of the devices of Fig. 4.
    - Fig. 6a 6c illustrate the steps of the method of the present invention.

15

- Figs. 7a 7c illustrate the steps of fabricating organic light emitting diodes using ink-jet printing.
- Figs. 8a 8c illustrate the fabrication of red green and blue devices on a common substrate.
- Figs. 9a 9c illustrate the use of ink-jet printing for fabricating bottom contacts.
  - Figs. 10a-10c illustrate fabrication of top contacts using ink-jet printing.
  - Figs. 11a 11c illustrate the use of ink-jet printing to fabricate three color OLEDs.
- Figs. 12a 12d illustrate the use ink-jet printing to fabricate a passive matrix.
  - Figs. 13a 13c illustrate the fabrication of an active matrix.
  - Figs. 14 (a) (b) illustrate the formation of thin film field effect transistors.
  - Fig. 15 illustrates a modified method of fabricating OLED devices

#### -6-DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a method of fabricating semiconductor devices, such as OLED's by ink-jet printing patterned luminescent polymer films.

5

10

15

20

25

30

In an example of the method of the present invention, the ink-jet printer used was a Cannon PJ-1080A Color Ink-Jet Printer with a resolution of 640 dots per line. This printer uses piezoelectric technology to squirt ink droplets from a nozzle with a 65-µm opening. There are four ink cartridges and four nozzles enabling the printer to print four different colors simultaneously. As the printer head scans the page and the piezoelectric materials are pulsed, ink is squirted from the nozzles onto the page. The only modification to the ink-jet printer for printing OLED's was to replace the ink cartridges with polymer solutions. Ink jet printing has previously been used to manufacture color-filters for Liquid Crystal Displays, but not to apply luminescent polymers.

The organic materials used were similar to those used by Wu, et al., IEEE Trans. Electron Devices 44, 1269 (1997), using doped polymer blends deposited by spin-coating, in which OLED's with over 1% external quantum efficiency and brightness of 4000 cd/m<sup>2</sup> were produced. The hole-transport polymer polyvinylcarbazol (PVK) and light emitting dyes coumarin 6 (C6), coumarin 47 (C47) and nile red were dissolved into chloroform solution, which was then deposited by ink-jet printing, or spin coating for comparison. After deposition, the chloroform evaporates leaving a doped polymer material. Typical concentrations of PVK dissolved in chloroform were 10g/l, and dye dissolved in chloroform were 0.1g/l, yielding on the order of 1% dye in the PVK. These concentrations are less than those used for spincoating, which were typically 15.4g/l PVK in chloroform and 0.05g/l dye in chloroform, yielding on the order of 0.3% dye in the PVK. In this initial ink-jet printing work, no electron transport agent was used. PVK, which had a high weightaverage molecular weight  $M_w$  of 1 100 000 g/mole reported by the supplier, was purchased from Aldrich Chemical Inc. and used as received. Green dye C6 and blue dye C47 were purchased from Lambda Physik Inc. Nile red was purchased from Aldrich. Chloroform solutions containing different amounts of PVK and luminescent materials were prepared by stirring and were passed through 0.45-µm filters. Ink-jet

-7-

printed thin films were printed onto 175-µm thick flexible polyester coated with indium tin oxide (ITO). Before deposition, the ITO was treated with an oxygen plasma to modify its surface properties for OLED's.

5

10

15

20

25

30

Fig. 1(a) and 1(b) show an optical micrograph of a number of ink-jet printed dots and a surface profile of the shape of a typical dot. The thickness of the dots ranged from 400 to 700 Angstroms and the dot widths ranged from 150 to 200 μm. The larger diameter dots tended to be thicker, indicating thickness variation is due to the total amount of deposited solution. In the optical micrograph of Fig. 1(a), some structure can be seen within the dot, which may be evidence of some mass transport due to segregation as the solvent evaporated. To demonstrate the ability of the ink-jet printing technique to deposit patterns, PVK doped with C6 dye was deposited with an ink-jet printed test pattern. This substrate was then illuminated using ultra violet excitation, and a photograph, Fig. 2, was taken of the red emission of the patterned polymer. A filter was used to cut out most of the 420nm polyester/PVK luminescence. During the experiment the ink-jet printer was operated in the "bold" mode, which causes the printer to print every dot twice, which is why the letters appear double.

Fig. 3 shows the photoluminescence spectra of three individual ink-jet printed thin films and spin-coated films made from the same solution, each with a different dye. The spin-coated films were spun-on at a speed of 4000 rpm for 60s. The photoluminescence was measured using a Perkin-Elmer LS50 luminescence spectrometer with an excitation  $\lambda$  of 380 nm for the C47 doped film and 440 and 520 nm for C6 and nile red doped films, respectively. No significant difference in shape or magnitude is seen between the films prepared by ink-jet printing vs. spin coating. It should be noted that the peak of 420nm in the C47 spectra is due to a combination of the polyester substrate and the PVK host, not the deposited film. The dye luminescence appears as a peak at 450nm on the shoulder of the 420nm peak.

It was difficult to fabricate devices directly on top of the polymer dots fabricated by ink-jet printing because of the difficulty in aligning a shadow mask for metal cathode formation directly over a polymer dot. Therefore to fabricate test devices the ink-jet printer was operated in a mode to create a continuous sheet of polymer rather than discrete dots. After ink-jet printing, the samples were loaded into

-8-

a vacuum chamber with a base pressure of <10<sup>-7</sup> torr for the metallization step of device fabrication. Typically, at least ~90 min were allowed between loading of samples and metal evaporation, and no further heating of samples was done. Top metal cathodes were deposited through a shadow mask to form an array of 250-μm diameter devices on the polymer film. Metal alloys such as Mg : Ag (10:1) were deposited by co-evaporation from two separate sources, followed by the deposition of Ag as a protective layer. The ITO on the polyester sheet served as the anode. The devices were then measured in air without any protective coating.

5

10

15

20

25

30

Fig. 4 shows the I-V curves of typical devices made by this procedure and a control device fabricated on a film spin-coated from the same polymer solution. The organic film thickness of the control device was about 50 nm. Current densities of ~mA/cm² are achieved at a voltage of ~7V for the control device, and ~6-11V for the ink-jet printed devices. Almost all of the voltages are lower than the drive voltage of ~10-11V seen in <u>Wu</u>, et al. on doped PVK devices without an electron transport agent, but in <u>Wu</u>, et al. the organic thickness was ~100nm. Fig. 5 shows the L-I characteristic of the two devices, which shows that the efficiency of the ink-jet printed device is about a factor of two less efficient than the spin coated device.

The methods of the present invention directly deposit the desired organic or other layers in the desired pattern using inkjet printing. In these methods, a liquid containing the desired materials or a precursor of the materials is deposited into a pattern. The liquid evaporates leaving the desired materials, or a precursor, which may be converted to the desired material, behind.

Patterning organics is important for color displays, in which separate red, green and blue devices are desired. When each devices made adjacent to each other, it is desirable to pattern 3 separate organic layers, each of which is typically first deposited over the entire surface, into three separate regions for the red, green and blue devices.

As more particularly shown in Fig. 6 (a), droplets 12 of organic containing liquid carriers are deposited from an ink-jet printer in a local area on the surface of a substrate 10. As shown in Fig. 6(b), the liquid carriers evaporate to create local regions 14 of desired organic film. The steps of Figs. 6(a) - 6(b) are repeated as shown in Fig. 6(c), with a droplet 16 incident on a new region of the substrate to create

-9-

another organic region.

5

10

15

20

25

30

The methods of Fig. 6(a) - (c) are used in Fig. 7(a) - (c) to fabricate organic light emitting diodes. A substrate 18 and bottom electrode 20 (which may be the same structure) is shown in Fig. 7(a). The electrode may be patterned for individual electrical control. Organic "islands" 22, 24, Fig. 7(b) are deposited on the substrate 18 by ink-jet printing. Electrodes 26, 28 are applied on top of the areas 22, 24, of organic material on the substrate 18 by evaporation, through shadow masks.

Fig 8 (a) - (b) illustrate fabrication of red, green and blue devices on the same substrate. As shown in Fig. 8(a), a substrate 30, such as glass, and bottom electrode 32 similar to that shown and described in connection with Fig. 7(a) is prepared. In Fig. 8(b), organic "islands" 34, 36, 38 of three different types are placed on the substrate 30 by ink jet printing using three different solution types, as red, green and blue inks are used in a conventional ink-jet printer for color printing on paper. Top contacts 40, 42, 44 in Fig. 8(c), are applied to each area of organic material in a manner similar to that shown and described in connection with Fig. 7(c). In these devices, either the bottom or the top electrode or both may be patterned for individual electrical control. Each "island" of organic material may be formed by a single incident droplet, or several droplets, either directly on top of each other or laterally of each other.

Figs. 9(a) - (c) show fabrication of bottom contacts in a pattern using ink-jet printing. The organic "islands" may be formed using ink-jet printing as previously discussed in connection with Figs. 6-8. As shown in Fig. 9(a) bottom contact 46 is formed on a substrate 48 by ink-jet printing. As shown in Fig. 9(b), organic materials 50 may be deposited onto the contact 46 by ink-jet printing in a desired pattern. As shown in Fig. 9(c) the top 52 contact may be deposited on the organic 50 by ink-jet printing.

Figs. 10(a) - (c) show fabrication of top contacts in a pattern using ink-jet printing. Fig. 10(a) illustrates the creation of the bottom electrodes 56, which may be created in a pattern on substrate 54. Fig. 10(b) shows the deposition of organic layers 58 onto electrodes 56 by ink-jet printing. As shown in Fig. 10(c), the top electrodes 60, 62 is deposited in a pattern by ink-jet printing over the organic layers 58.

5

10

15

20

25

30

PCT/US99/01914

In connection with Figs. 9 and 10, the contacts may be formed of a precursor of the final metal, metal particles suspended in a solvent, a supersaturated solution which will yield solid metal (such as the Rochelle salt method), or an organic with good conductivity.

The techniques of Figs 9 and/or 10 may be combined with the steps described in Figs. 6-8. Figs. 11 (a) -(c) illustrates the fabrication of three color OLED's with individual top contacts by ink-jet printing. Fig. 11(a) shows a substrate 64 formed with bottom electrodes 66. The bottom electrodes may be patterned. As shown in Fig. 11(b), three types of organic, red, blue, and green, 68, 70, 72 are deposited by ink-jet printing. Fig. 11(c) illustrates the formation of top contacts 74, 76, 78 on the organic islands 68, 70, 72, respectively by ink-jet printing.

Figs. 12(a) - (d) show formation of a passive matrix using the methods of the present invention. In Fig. 12(a), bottom electrode lines 80, 82, 84 are formed in one direction on substrate 86. As shown in Fig. 12(b), polymer islands 88, 90 are applied on top of the bottom electrode lines 80, 82 in regions to be crossed by the top electrode. These polymer islands 88, 90 may be of different emitting colors for a color display matrix. As shown in Fig. 12(c), the top contact lines 92 are applied perpendicular to the bottom contact lines. The final matrix thus produced is shown in Fig. 12(d).

Figs. 13 (a) - (c) shown the formation of an active matrix using the methods of the present invention. In Fig. 13(a), individual bottom electrode surfaces 96, 98, 100 are formed on a substrate 94 and may be insulated from each other as shown at 102, 104, 106. These bottom electrodes may be connected to circuitry (not shown) which enables the bottom electrodes to be individually addressable. As shown in Fig. 13(b), organic "islands" 108, 110, 112 are deposited by ink-jet printing onto exposed bottom electrodes. These "islands" may be of different emitting color for a color matrix. As shown in Fig. 13(c), the top electrode 114 (Al:Li or Mg:Ag) is applied over the "islands". The top electrode need not be patterned.

Figs. 14 (a) - (b) illustrate the formation of thin film field effect transistors with organic as the semiconducting layer. Fig. 14 (a) shows a substrate 116 on which gate electrode 118 is formed. Gate electrode 118 may be metal or a conducting polymer.

-11-

Gate insulator 120 is formed over the gate electrode 118. Insulator 120 may be formed of organic or inorganic material. In Fig. 14 (b), a polymer semiconducting layer 122 of poly-thiophene, for example, is formed by ink-jet printing over insulator 120. Source/ drain contacts 124, 126 are formed on semiconducting layer 122 by conventional methods. Contacts 124, 126 may be formed of gold or a conducting polymer. The source/drain contacts 124, 126 may be formed before forming the polymer semiconducting layer 122. Further, the gate insulator 120 be also be formed by ink-jet printing of a material such as polyamide.

5

10

15

20

Fig. 15 illustrates a modified method of fabricating OLED devices. Substrate 128 has bottom contact 130 formed thereon. Bottom contact 130 may be patterned. Insulator 132, 134 formed thereon. Organic material 136 is formed by ink-jet printing over the insulator 132, 134. Top contact 138 is formed over organic 136. The top contact 138 may be patterned. In this approach, where insulator 132, 134 is patterned over the bottom contact 130, the patterned insulator may adjust the wetting and drying of the liquid drop applied by ink-jet printing. The patterned insulator 132, 134 also restricts the OLED to a small portion of the final polymer dot. In both of the foregoing cases, thickness of the polymer in the final active OLE device is controlled as desired.

Having thus described the invention in detail, it is to be understood that the foregoing description is not intended to limit the spirit and scope thereof. What is desired to be protected by Letters Patent is set forth in the appended claims.

#### -12-CLAIMS

#### What is claimed is:

- 1. A process for forming a pattern on a substrate by deposition of an organic material comprising the steps of:
- depositing organic material in a solvent onto a substrate by ink-jet printing; and evaporating the solvent, whereby said organic material remains on the substrate.
- 2. The process of claim 1, further comprising drying the deposited material to remove said solvent.
  - 3. The process of claim 1 wherein said organic material is semiconducting.
  - 4. The process of claim 1 wherein said organic material is insulating.
  - 5. The process of claim 1 wherein said organic material is conducting.
  - 6. The process of claim 1 wherein said organic material is a luminescent
- polymer.

20

- 7. The process of claim 1 wherein said material includes polyvinylcarbazol film.
- 8. The process of claim 1 wherein said solvent is chloroform.
- 9. The process of claim 1 wherein said material includes light emitting dyes.
- 10. The process of claim 9 wherein said light emitting dyes include coumarin and nile red.
- 11. The process of claim 10 wherein said coumarin is coumarin 6.
  - 12. The process of claim 10 wherein said coumarin is coumarin 47.
  - 13. The process of claim 10 wherein said coumarin is coumarin 6 and coumarin 47.
- 14. The process of claim 1 wherein said organic material is a mixture of polymers25 and other organic molecules.
  - 15. A process for making organic light emitting diodes comprising the steps of : depositing organic material in a solvent onto a substrate by ink-jet printing; and evaporating the solvent, said organic material remaining on the substrate.
- 16. The process of claim 15 wherein said depositing step operates an ink-jet printer in a mode to create a continuous sheet of polymer.

-13-

- 17. The process of claim 16 further including the step of metallizing said ink-jet printed substrates.
- 18. The process of claim 17 further including the step of depositing with ink-jet printing top metal contacts on said substrate.
- 5 19. The process of claim 18 wherein said top metal contacts are deposited through a shadow mask.
  - 20. The process of claim 15 further including the step of depositing with ink-jet printing bottom metal contacts on said substrate.
- 21. The process of claim 18 wherein said top metal contacts are deposited in a pattern.
  - 22. The process of claim 20 wherein said bottom metal contacts are deposited in a pattern.
  - 23. The process of claim 15 further wherein said organic material includes light emitting dyes.
- 15 24. The process of claim 23 further including the step of depositing top contacts on said organic material by ink jet printing.
  - 25. The process of claim 24 further including the step of depositing bottom contacts on said substrate by ink-jet printing.
- 26. A process of forming a passive matrix comprising the steps of:
  depositing electrode lines on a substrate by ink-jet printing;
  depositing organic polymers onto said electrode lines by ink-jet printing; and
  depositing top contacts onto said organic polymers by ink-jet printing, said
  organic polymers being deposited in regions to be crossed by said top contacts.
- A process of forming an active matrix comprising the steps of:
   depositing bottom electrodes onto a substrate by ink jet printing;
   depositing organic polymers onto said bottom electrodes;
   depositing top electrodes onto said organic polymers; and
   connecting said bottom electrodes to circuitry for individually addressing said
   bottom electrodes.
- 30 28. The process of claim 37 wherein said bottom electrodes are insulated from each other in a predetermined pattern.

-14-

29. A process of forming thin film field effect transistors comprising the steps of:

forming a gate electrode on a substrate;

forming a gate insulator over said gate electrode;

forming a polymer semiconducting layer on said insulator by ink-jet printing;

5 and

10

forming source and drain contacts on said semiconducting layer.

- 30. The process of claim 29 wherein said gate insulator is formed by ink-jet printing, and the semiconducting layer by other techniques.
- 31. The process of claim 29 wherein the source and drain contacts are applied directly on the gate insulator before the semiconducting layer is deposited.
- 32. The process of claim 30 wherein the source and drain contacts are applied directly on the gate insulator before the semiconducting layer is deposited.
- 33. The process of claim 29 wherein the semiconducting layer comprises a non-polymeric organic film or a polymer/small organic molecule blend.
- 15 34. The process of claim 30 wherein the semiconducting layer comprises a non-polymeric organic film or a polymer/small organic molecule blend.
  - 35. The process of claim 31 wherein the semiconducting layer comprises a non-polymeric organic film or a polymer/small organic molecule blend.

1/12

FIG. 1A

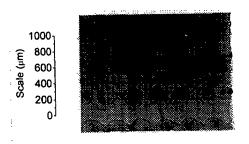


FIG. 2



FIG. 1B

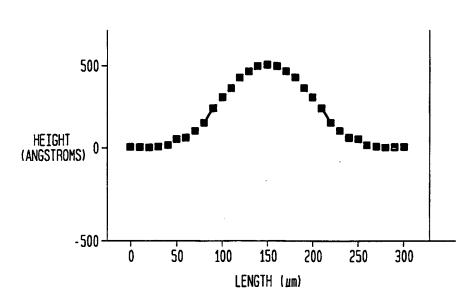
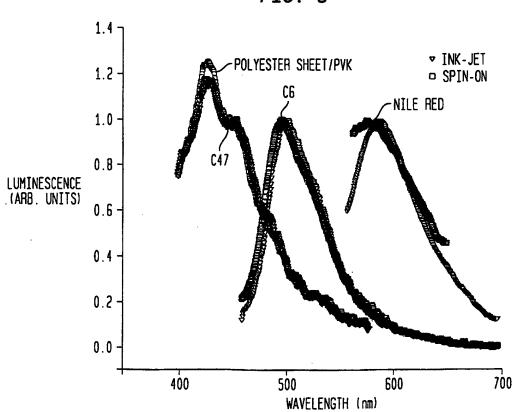


FIG. 3



SUBSTITUTE SHEET (RULE 26)

3/12

FIG. 4

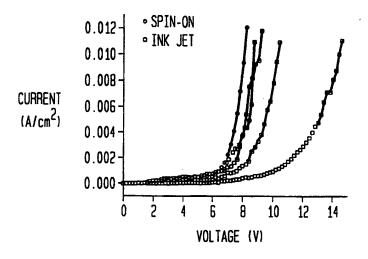
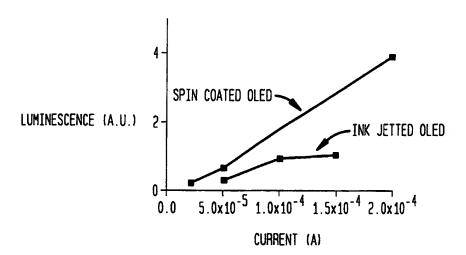


FIG. 5



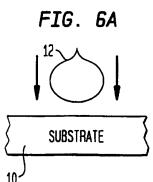


FIG. 6B

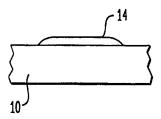


FIG. 6C

FIG. 7A

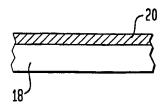


FIG. 7B

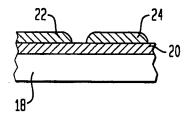


FIG. 7C

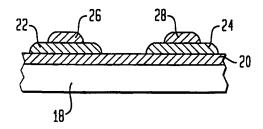


FIG. BA

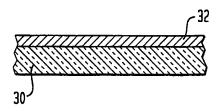


FIG. 8B

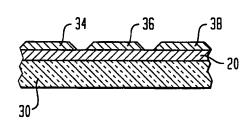


FIG. BC

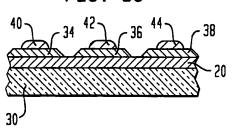
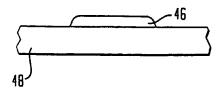
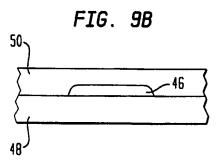


FIG. 9A





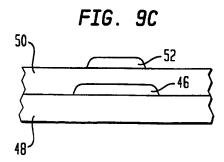
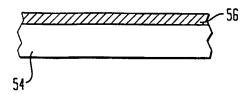
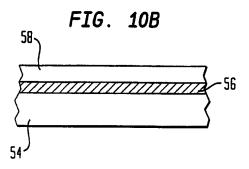


FIG. 10A





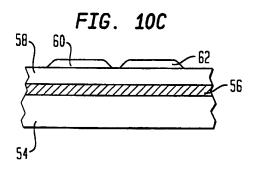


FIG. 11A

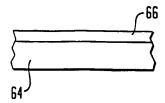


FIG. 11B

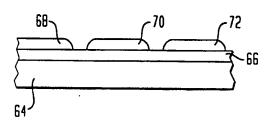
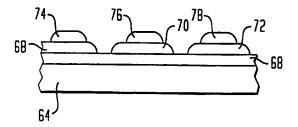


FIG. 11C



10/12

FIG. 12A

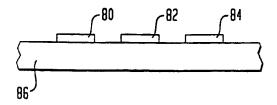


FIG. 12B

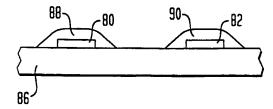


FIG. 12C

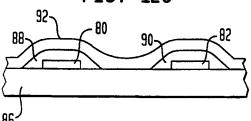
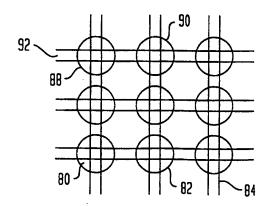


FIG. 12D



SUBSTITUTE SHEET (RULE 26)

FIG. 13A

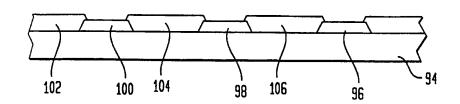


FIG. 13B

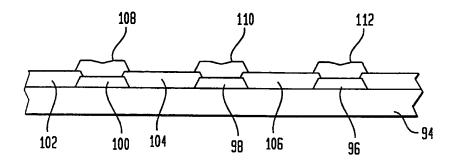
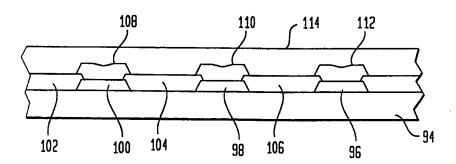
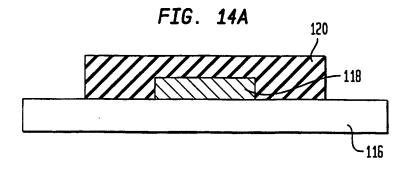
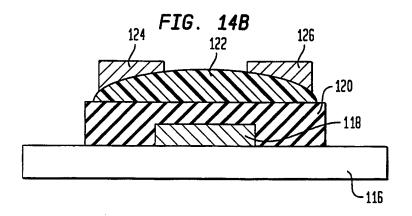
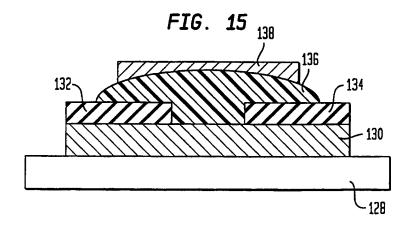


FIG. 13C









Substitute for form 1449A/PTO				Complete if Known		
				Application Number	10/541,956	
	INFORMATION D	ISCLOSU	RE	Filing Date	10/31/2005	
	STATEMENT BY APPLICANT			First Named Inventor	Wolfgang Clemens	
				Group Art Unit	2811	
(Use as many sheets as necessary)		Examiner Name	Arora, Ajay			
Sheet	1	Of	3	Attorney Docket Number	411000-137	

Examiner	Cite	Document Number	Publication- Date	Name of Patentee or	Pages, Columns, Lines, Where
Initial*	No.1	Number-Kid Code <sup>2 (f known)</sup>	MM-DD-YYYY	Applicant of Cited Document	Relevant Passages or Relevant Figures Appear
		US-3,999,122	12-21-1976	Winstel et al.	All references cited are cited in co-pending applications or were cited by the Examiner of the co-pending applications
		US-4,246,298	01-20-1981	Guamery	
		US-4,340,057	07-20-1982	Bloch	
		US-4,554,229	11-19-1985	Small	
		US-4,865,197	0912-1989	Craig	
		US-4,937,119	06-26-1990	Nickels et al.	
		US-5,075,816	12-24-1991	Stormbom	
***		US-5,705,826	01-06-1998	Aratani et al.	
		US-5,364,735	11-15-1994	Akamatsu	
		US-5,625,199	04-29-1997	Baumbach et al.	
		US-5,693,956	12-02-1997	Shi	
		US-5,705,826	01-06-1998	Aratani	
		US-5,883,397	03-16-1999	Isoda et al.	
		US-5,994,773	10-30-1999	Hirakawa	
		US-5,998,805	12-07-1999	Shi et al.	
		US-6,072,716	06-06-2000	Jacobsen et al.	
		US-6,150,668	11-21-2000	Bao	
		US-6,180,956	01-30-2001	Chondroudis	
		US-6,221,553	04-24-2001	Wolk	
		US-6,329,226	12-11-2001	Jones	
		US-6,330,464	12-11-2001	Colvin	
		US-6,362,509	03-26-2002	Hart	
		US-6,384,804	05-07-2002	Dodabalapur et al.	
		US-6,498,114	12-24-2002	Amundson et al.	
		US-6,518,949	02-11-2003	Drazic	
		US-6,521,109	02-18-2003	Bartic et al.	
		US-6,548,875	04-15-2003	Nishiyama	
		US-6,556,840	04-29-2003	Hudson	
		US-6,593,690	07-15-2003	McCormick	

Substitute for form 1449A/PTO			Complete if Known		
INFORMATION DISCLOSURE				Application Number	10/541,956
				Filing Date	10/31/2005
STATEMENT BY APPLICANT			NT	First Named Inventor	Wolfgang Clemens
				Group Art Unit	2811
(Use as many sheets as necessary)		)	Examiner Name	Arorra, Ajay	
Sheet 2 Of 3		3	Attorney Docket Number	411000-137	

US-6,603,139	08-05-2003	Tessler	
US-6,621,098	09-16-2003	Jackson	
US6,960,489	11-01-2005	Bernds et al.	

Examiner	Cite	Foreign Patent Document	Publication- Date	Name of Patentee or	Pages, Columns, Lines,	
Initial*	No.1	Country Code <sup>3</sup> Number <sup>4</sup> Kind Code <sup>5 (if known)</sup>	MM-DD-YYYY	Applicant of Cited  Document	Where Relevant Passages or Relevant Figures Appear	Τŧ
		DE 101 20 686	11-07-2002	Siemens AG		
		DE 101 20 687	10-31-2002	Siemens AG	-	
		DE 198 51 703	05-04-2000	Institute fur Halbleiterphysik		
		DE 692 32 740 T2	04-29-1993	Motorola, Inc.		
		EP 0 108 650	05-16-1984	Zytrex Corporation		X
		EP 0 418 504	03-27-1991	Matsushita		х
		EP 0 603 939 A2	06-29-1994	Philips Electronics N.V.		×
		EP 0 690 457	01-03-1996	Al-Coat Lts.		Х
		EP 0 786 820	07-30-1997	Motorola		х
		EP 1 113 502	07-04-2001	Seiko Epson Corp.		×
		JP 03290976 A	12-20-1991	Kamiyana Kenichi		х
		JP 62065472 A	03-24-1987	Toshiba Corp.		х
		WO 02/47183	06-13-2002	Siemens AG		
		WO 02/47183 (abstract)	06-13-2002	Siemens AG		х
		WO 020/99907 (abstract)	12-12-2002	Siemens AG		×
		WO 02/091495	11-14-2002	Coatue Corp.		х
		WO 03/036686	05-01-2003	The Gov't of the USA		×
		WO 99/30432	06-17-1999	Koninklijke Philips		×
		WO 99/39373	08-05-1999	Trustees of Princeton U		X

Substitute 1	for form 1449A/PTO		Com	plete if Known
			Application Number	10/541,956
	INFORMATION DISCL	.OSURE	Filing Date	10/31/2005
	STATEMENT BY APPLICANT  (Use as many sheets as necessary)		First Named Inventor	Wolfgang Clemens
Ì			Group Art Unit	2811
			Examiner Name	Arora, Ajay
Sheet	Sheet 3 3		Attorney Docket Number	411000-137+

#### NON PATENT LITERATURE DOCUMENTS

Examiner	Cite	looked many of the pathon (in CADITAL LETTEDO) by a file of the pation (the particular) title of the in-	Τ
Initial*	No.1	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	T²
		ANGELOPOULOS M et al., "In-Situ Radiation Induced Doping", Mol. Crystl. Liq. Cryst., 1990, vol. 189, pp 221-225.	x
		DRURY et al., "Low-Cost All-Polymer Integrated Circuits", American Institute of Physics, Applied Physics Letters, 1998, Vol. 73, No. 1, pp 108—110, July 6, 1998.	x
		FORREST et al.: "The Dawn of Organic Electronics", IEEE Spectrum, August 2000 (2000-08), Seiten 29-34, XP002189000, IEEE Inc., New York, US ISSN:0018-9235, Seite 33, rechte Spalte, Zelle 58-Seite 34, linke Spalte, Zeile 24; Abbildung 5.	X
		GARBASSI F., et al., "Bulk Modifications", Polymer Surfaces, John Wiley & Sons, 1998, pp 289-300.	×
		GARNIER, F. et al, "All-Polymer Field-Effect Transistor Realized by Printing Techniques", Science, American Association for the Advancement of Science, US, vol 265, 16 September 1994, pp 1684-1686.	х
		GONCALVES-CONTO, Sylvie, et al., "Interface Morphology in Organic Light-Emitting Diodes", Advanced Materials 1999, Vol 11, No. 2, pp 112—115.	х
		HERGEL, H. J.: "Pld-Programmiertechnologien", Elektronik, Franzis Verlag GMBH. Munchen, DE, Bd 41, Nr. 5, 3. Marz 1992 (1992-03-03), Seiten 44-46, XP000293121, ISSN: 0013-5658, Abbildungen 1-3.	
		KUHLMANN et al., "Terabytes in Plastikfolie", Organische Massenspeicher vor der Serienproduktion	
		NALWA, H.S., "Organic Conductive Milecules and Polymers", Vol, 2, 1997, pp 534 – 535.	x
		SPEAKMAN, S.P. ET AL., "High performance organic semiconducting thin films: Ink Jet printed polythophene [rr-P3HT], Organic Electronics 2 (2), 2001, pp. 65 – 73.	x
		ZANGARA L., "Metall Statt Halbleiter, Programmierung Von Embedded ROMS Ueber Die Metallisierungen", Elektronik, Franzis Verlag GmbH, Munchen, DE, Vol. 47, No. 16, Aug. 4, 1998, pp 52—55.	
		ZIE VOOR TITEL BOEK, d 2e PAGINA,XP-002189001, pg 196-228.	х

Examiner Signature	Date Considered	

<sup>\*</sup>EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

<sup>1</sup> Applicant's unique citation designation number (optional). 2 Applicant is to place a check mark here if English language Translation is attached.

This collection of information is required by 37 CFR 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450**.

# This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

BLACK BORDERS

IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

FADED TEXT OR DRAWING

BLURRED OR ILLEGIBLE TEXT OR DRAWING

SKEWED/SLANTED IMAGES

COLOR OR BLACK AND WHITE PHOTOGRAPHS

GRAY SCALE DOCUMENTS

LINES OR MARKS ON ORIGINAL DOCUMENT

REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

## IMAGES ARE BEST AVAILABLE COPY.

**☐** OTHER: \_\_\_\_\_

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.